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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

THE SIGNIFICANCE OF CHANGING ATOMIC VOLUME.

II. — *THE PROBABLE SOURCE OF THE HEAT OF CHEMICAL COMBINATION, AND A NEW ATOMIC HYPOTHESIS.*

By Theodore William Richards.

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I. Presentation of the Facts.

In a paper first presented to the American Academy of Arts and Sciences in May, 1900, then revised and printed in the Proceedings a year later,* certain interesting facts concerning the significance of changing atomic volume were pointed out and emphasized. It was shown that the contractions and expansions occurring in liquids and solids during chemical reaction are related to the affinities concerned, as nearly as we can estimate those affinities. A greater affinity seems to produce a greater contraction, if the compressibilities concerned are equal. It seemed possible that this idea might have very fundamental and far reaching applications as to matters of fact, and might lead moreover to a somewhat new conception of the atomic hypothesis.

Many such applications have already been tested with plausible results. The complete detailing of the ramifications of this idea would need the compass of a book; in the present paper the attempt will be made merely to sketch the relations of a single side of the question.

In the paper already referred to the suggestion was made that the heat of chemical reaction might be traceable to the work done by chemical affinity in compressing the substances concerned. The discussion below will show the close relationship which exists between these facts.

The most serious difficulty in the way of determining the relationship is the extreme scarcity of data concerning compressibility. Obviously

* These Proceedings, 37, 1 (June, 1901).

the compressibility of a *compound* contains too many possible variables to form at once the certain basis of exact reasoning; and among *elements* only mercury, lead, copper, and iron in the uncertain form of steel, seem to have been even crudely studied.* The problem is moreover complicated by the fact that the coefficient of compressibility diminishes as the pressure increases.

The work which is needed in order to compress a given substance to a given extent can only be computed accurately when the varying compressibility through the whole range is known; and since the pressures involved in the present question are clearly many thousands of atmospheres, the precise solution of the problem seems to be a distant matter, although by no means impossible.

By a process of approximation some light may be obtained, however. If one selects a single series of compounds, such as the chlorides, it is obvious that a large part of the compressibility throughout the series should correspond to the compressibility of the chlorine. In those cases where the compressibility of the metal is smallest, the change of volume would be due almost solely to the compression of the non-metal.

In view of these considerations, the first approximation should be obtained by comparing the actual contractions taking place during the formation of amounts of substance containing the same weight of chlorine with the heat evolved in each case. The starting point in each case is liquid chlorine, having a molecular volume of about 50 (or an atomic volume of about 25) at 20°. The heat of formation of the chloride is usually given in tables of data as starting from chlorine gas, under atmospheric pressure; hence the latent heat of evaporation and expansion of the chlorine should be subtracted from the usual values in order to institute a precise comparison.† However, these quantities cannot be large in proportion to the heat of combination with the metal, and they

* Landolt and Börnstein, Phys. Chem. Tab., pp. 268, 278 (1894). Unless otherwise stated, all data used in this paper were taken from this admirable book of tables.

† The latent heat might be approximately calculated from the data of Knietsch (Landolt and Börnstein, p. 80 (1894)) as follows: —

$$Q = \frac{R\,T^2\,dP}{P\,dT} = \frac{8.32 \times (293.5)^2 \times 0.19}{6.62 \times 1} = 20{,}500 \text{ joules, or } 20.5$$

kilojoules, between 20° and 21° C, for the evaporation of one gram-molecule. The wide deviations from the gas-law exhibited by chlorine render the calculation very uncertain. It is enough, however, to show that the value is relatively small. The heat absorbed on expansion must also be in doubt on account of the same deviations.

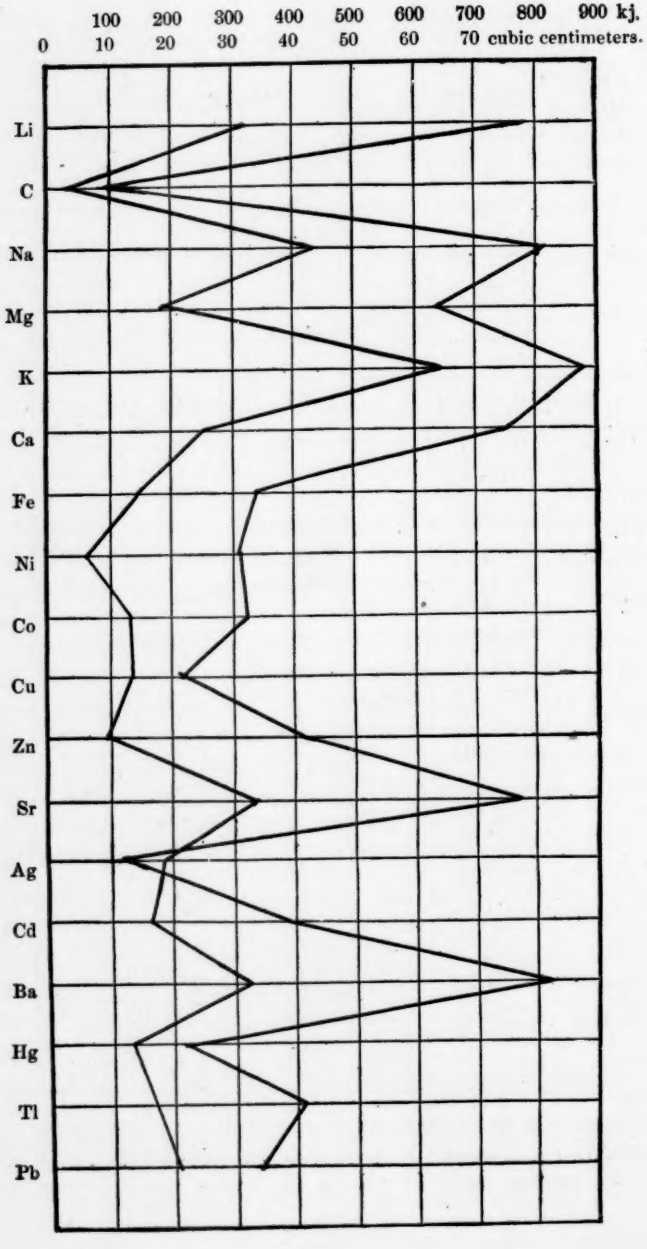
would apply equally in each case; hence in the first approximation the usual values for the heats of combination may be given without affecting the argument.

The table of data herewith collected compares the contraction which takes place when two gram-atoms of chlorine combine with some other substance, and the heat evolved during the operation.

COMPARISON OF CONTRACTION WITH HEAT OF FORMATION INVOLVED IN THE SYNTHESIS OF CHLORIDES.

Metal.	Atomic Volume of Metal.	Atomic Vol. Metal + n times Atomic Vol. Chlorine.	Molecular Volume of Chloride.	Difference or Contraction.	Contraction corresponding to 2 Atoms Chlorine.	Heat of Formation corresponding to 2 Atoms Chlorine. (Kilojoules.)
Lithium .	11.9	36.9	20.9	16.0	32.0	784
[Carbon^{IV}] .	3.4	103.4	96.5	6.9	3.5	99
Sodium . .	23.7	48.7	27.2	21.5	43.0	816
Magnesium	13.3	63.3	43.9	19.4	19.4	632
Potassium .	45.5	70.5	37.8	32.7	65.4	872
Calcium .	25.3	75.3	50.0	25.3	25.3	760
Iron^{II} . .	7.1	57.1	42.6	14.5	14.5	343
Nickel . .	6.7	56.7	50.4 (?)	6.3	6.3	312
Cobalt . .	6.7	56.7	44.2	12.5	12.5	320
Copper . .	7.1	57.1	44.1	13.0	13.0	216
Zinc . . .	9.5	59.5	49.6	9.9	9.9	407
Strontium .	34.5	84.5	51.9	32.6	32.6	772
Silver . .	10.3	35.3	26.5	8.8	17.6	123
Cadmium .	13.0	63.0	46.5 (?)	16.5	16.5	390
Barium . .	37.0	87.0	53.9	33.1	33.1	815
Mercury^{II} .	14.7	64.7	50.0	14.7	14.7	223
Thallium .	17.2	42.2	34.1	8.1	16.2	406
Lead . . .	18.2	68.2	48.1	20.1	20.1	346

The parallelism of the heat of reaction and the contraction which results from it, is obvious from the table and the accompanying diagram,


100 200 300 400 500 600 700 800 900 kj.
0 10 20 30 40 50 60 70 cubic centimeters.
Li
C
Na
Mg
K
Ca
Fe
Ni
Co
Cu
Zn
Sr
Ag
Cd
Ba
Hg
Tl
Pb

which represents graphically the results recorded in the table. The elements are arranged in the order of their atomic weights, and both sets of data are drawn as abscissae, because this method of treatment will facilitate later comparison, and because it obviates certain irregularities due to periodicity. Each division stands for ten cubic centimeters of contraction on the left hand curve, and a hundred kilojoules of heat-energy on the right hand curve.

The correspondence is obviously too close to be the result of chance. One is forced to believe that a fundamental relationship exists between the two phenomena.

In these curves the compressibility is ascribed wholly to chlorine, and that of the other substance is neglected; but when the latter is large, it also must enter into the problem. Unfortunately our data concerning compressibility are unusually limited; but approximate calculations, based upon such as are known or may be guessed, show that at least some of the irregularities in the parallelism may be ascribed to this source.

We may thus formulate the following law: *The work needed for the compression involved in the formation of one solid or liquid by the combination of two others is approximately proportional to the heat evolved.*

While the general tendency of the law is manifest, and a correction for individual compressibilities would undoubtedly make it more so, there are nevertheless several exceptions to be explained. These may arise from several causes; in the first place, many specific gravities of solids are known only approximately; * in the next place, it is important that the same modifications of each substance should enter into each calculation. A plausible explanation has been found even for the exceptionally wide deviation exhibited by argentic chloride; but this point will not be dwelt upon now, since it is being submitted to the test of experiment.

The relation may be further illustrated by a table giving the data for a few bromides, and of course many other data might also be given. In order to eliminate as much as possible the contraction of the metal, it is well to choose for comparison a common non-metal possessing a comparatively large coefficient of compressibility, hence both chlorine and bromine serve well.

As a final example, the case of a single metal combining with several

* See Richards, These Proceedings, **31**, 163 (1895); also Ostwald, Zeitschr. phys. Chem. **3**, 143 (1889).

non-metals may be cited. Potassium is chosen in this last case because it is probably among the most compressible of metals.

COMPARISON OF CONTRACTION WITH HEAT OF FORMATION INVOLVED IN THE SYNTHESIS OF THE BROMIDES.

Metal.	Atomic Volume of Metal.	Atomic Vol. Metal + n times Atomic Vol. Bromine.	Molecular Volume of Bromide.	Difference or Contraction.	Contraction corresponding to 2 Atoms Bromine.	Heat of Formation corresp'd'g to 2 Atoms Bromine.
Sodium .	23.7	49.2	34.2	15.0	30.0	718
Potassium	45.5	71.0	44.2	26.8	53.6	796
Calcium .	25.3	76.3	60.1	16.2	16.2	648
Zinc . . .	9.5	60.5	53.4*	7.1	7.1	318
Strontium.	34.5	85.5	58.4*	27.1	27.1	659
Cadmium .	13.0	64.0	56.9	7.1	7.1	315
Barium .	37.0	88.0	62.2*	25.8	25.8	711

COMPARISON OF CONTRACTION WITH HEAT OF FORMATION INVOLVED IN THE SYNTHESIS OF POTASSIC HALIDES.

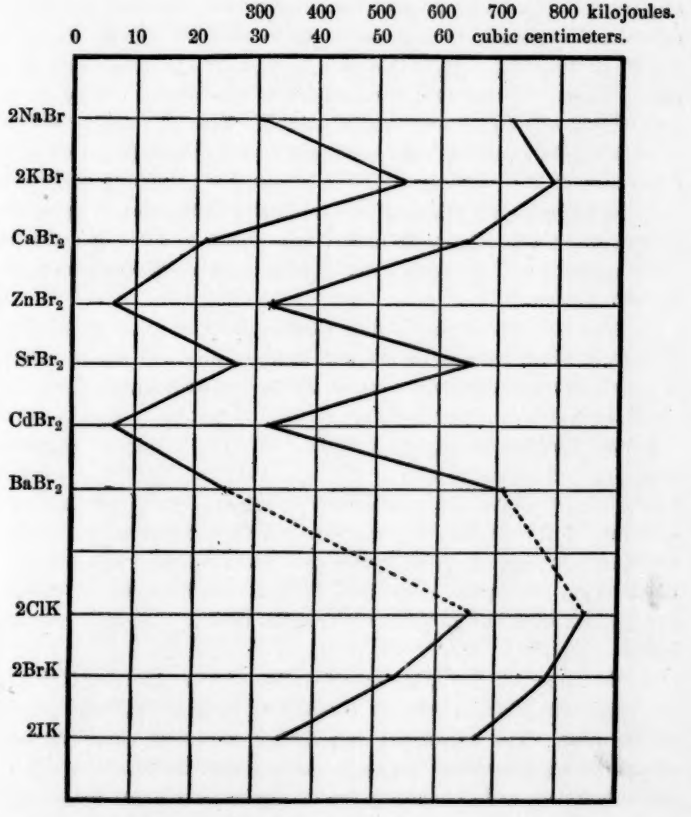
Halogen.	Atomic Volume of Halogen.	Sum of At. Vols. of Metal and Halogen.	Molecular Volume of Salt.	Difference or Contraction.	Heat of Formation of 2 Mols.
Chlorine .	25.0	70.5	37.8	32.7	$850 \pm$†
Bromine .	25.5	71.0	44.2	26.8	796
Iodine . .	25.7	71.2	53.8	17.4	670

When the more obvious experimental errors have been considered, two important questions at once suggest themselves: Does this proportionality signify equality, or is some of the energy of compression stored as potential energy and not manifested as heat? Again, if this equality exists, is it always exact, or is it modified by subordinate secondary effects?

* These values are calculated from very accurate determinations of specific gravity made recently in this Laboratory. See These Proceedings, **31**, 163 (1895).

† Approximately corrected for heat of evaporation and expansion.

These questions cannot be answered at present. The total amount of work done in any case cannot be computed without a knowledge of the compressibility of the substances involved throughout the total range of volume, as has already been said. Unfortunately no suitable data exist



capable of satisfying the conditions of the problem. Before long I hope to present such data, and to formulate answers to both questions; for the present the following unsatisfactory approximation is suggested as being better than nothing.

From the study of many allied data I have been able to form an approximate evaluation of the compressibilities of sodium and chlorine.

If one accepts these guesses, and imagines that the compressibilities decrease with decreasing volume according to the usual approximate law, one arrives at the conclusion that an amount of work equivalent to the heat of combination of sodium and chlorine would correspond to a change of volume in the system not far from the observed change of volume. The outcome is complicated by the fact that even in elements, but especially in compounds, there may be superposed several grades of compressibility. This can be explained hypothetically as follows: When the molecule is composed of two atoms, the highly compressed portion of each atom at the point of chemical union should have a much smaller coefficient of compressibility than the slightly compressed remainder of the molecule. If the molecule is polymerized, there will probably be yet other grades of compressibility in the various parts. The only object of a calculation so uncertain as this is to show that the heats of formation are of the same order of magnitude as the work involved in the compression.

In spite of the inevitable difficulties in the way of interpretation — difficulties which seem to be inherent in the problem — the presumption is strong that the *chief source of the heat of chemical combination is the work performed in compressing the material.* Since the heat of reaction is known to represent only approximately the free energy of the reaction, while the compression may really represent the affinities at work, one would hardly expect the relation to be exact. The generalization is a question of fact; it does not necessarily involve any atomic hypothesis, and can be regarded as uncertain only on account of the uncertainty of the data at present accessible. It is my intention to carry out the experimentation necessary to place the law on a more stable basis.

In the same way any other manifestation of attraction or affinity, such as cohesion or adhesion, should have a compressing effect and therefore evolve heat. The superficial and limited nature of these phenomena would ordinarily prevent any appreciable rise in temperature. In some cases, however, as in the adsorption of liquids and gases by porous material exposing a large surface, such a heating effect has been actually observed. Thus the essential difference between water of crystallization and adsorbed water is that the former penetrates the mass, while the latter is merely superficial.

It is obvious, moreover, that the same considerations apply to solidification and change of allotropic form. For example, liquid phosphorus, yellow phosphorus, and red phosphorus have at 44° the atomic volumes

17.66, 17.1, and about 14.1 respectively. The first small contraction is attended with an evolution of 0.65 kilojoules, and the second larger one with the evolution of 114 kilojoules of heat energy. In those cases where there is a transition from a more compressible union to a stabler, less compressible one, involving more work of compression, solidification would involve increase of volume, as in the case of water.

II. A Plausible Interpretation.

It becomes now an interesting question to determine, if possible, the mechanism by which this work is converted into heat. One is reminded at once of the compression of a gas, where the work of compression reappears quantitatively as heat energy. But the compression under consideration differs from the other in detail, because in the present case the attraction of the two substances for one another seems to be the cause of their mutual compression; and this mutual compression takes place not from the outside, but throughout the whole substance.

Those who shun the atomic hypothesis and consider substance only in the mass, will rest contented without further attempt at interpretation; but those who hold that the hypothesis is a useful tool, to be thrown aside when newer invention has devised a better one, will be tempted to go further.

The case, considered hypothetically, seems to be this: When two different atoms possessing mutual affinity approach one another, they are drawn closer than they can be to their respective fellows, and in the process evolve heat. The "repulsion" which is often supposed to surround an atom, and prevent it from touching any other, seems to be partially overcome by the potential energy of affinity. But of what nature is this "repulsion"? Ordinarily it is assumed to be due to the frequent impacts of a hard atom in the centre of the space; but no evidence is afforded of the existence of a free space. Indeed, it seems inconceivable that solids should retain their structure, or should be capable of retaining gases or liquids, if they are so loosely built up. A pile of sand would be stable compared to such a fabric.

The present research points to quite a different interpretation of the facts. The space occupied by a solid seems to have a *chemical* significance as well as a physical one; it seems, indeed, to be as essential a property of the material as any other property. Since the significance of the total volume is a chemical one, the "free space" around each individual atom must also have a chemical as well as a physical significance.

In other words, we have no right to imagine that the space is "free" or that there is a hard particle in the centre; the shell is as essential an attribute of the atom as the centre. But how are we to account for heat vibration, if the atom is supposed to fill the whole space? This question is important; but before answering we must consider some of the consequences of this form of compression.

Let us imagine two highly elastic spheres; for example, two very thin-walled india-rubber balls filled with gas. Imagine these to be drawn together by a powerful attraction resident throughout themselves. When they come in contact, each will compress the other and evolve heat in the process. They will remain bound together and distorted, unless some force separates them. If the shell of an atom is elastic and compressible, it is only reasonable to suppose that the interior is also. In that case the whole substance of both of two combining atoms will suffer distortion from the mutual attraction of every part of their substance; and the concentration of those constituents in each atom which cause the affinity will thus be increased in the half nearest the other atom. The supposition that the affinity comes from within will cause here an essential divergence from the actual conditions in two balls filled with gas, in which the gas is distributed equally throughout. As a consequence, the opposite half which is not combined will lose some of it attractive constituents, and should then have less tendency to unite with the new substances than it had before its union with the first atom. This plausible influence agrees with the well-known facts of "false equilibrium" and the nascent state; in fact, it would account in general for the permanence of slightly stable compounds.

By the process of hypothetical reasoning given above, one concludes that the *whole substance* of the atom may be elastic. In that case heat vibration might consist simply in alternate condensation and rarefaction of the medium within the shell, started by the momentum of impact. This would continue indefinitely, unless the vibration were imparted to other substances possessing less. Such internal rarefaction and condensation might well tend to distend the atom if any portion of the atom were held by another.

Thus, it is evident that there is no difficulty in imagining internal vibration in an atom which is packed on all sides closely with other atoms, or in explaining the mechanism of the thermal expansion of solids and liquids upon that basis. The chief reason for imagining a small hard particle with a large free space around it is therefore removed.

Two other reasons for retaining the conception of the old atom may be

urged; one, the continuity of the liquid and gaseous state, and the other, the porosity of solids.

In answer to the first, attention may be called to the fact that the continuity of the liquid and gaseous condition exists actually only at the critical pressure; below that point they are, as a matter of fact, discontinuous and very different. Perhaps the critical pressure is simply the point where the gas molecules at the critical temperature are pressed into actual contact. The compressibilities of very compressed gases are, in fact, of the same order of magnitude as those of liquids.

Porosity is usually only manifest under very great pressure, which might be enough to compress the atoms into smaller space, and thus open orifices which previously did not exist.

From these considerations it seems to me that the new kinetic conception of the solid and liquid state has no disadvantages which the old conception does not possess, while it has many advantages which the old theory has not.

But it is not the intention of the present paper to enter into the detail of so large a question. I hope that in the next few years I may be permitted to study and report upon the possible consequences of the significance of changing atomic volume.

In the preceding paper and the present one, the following phenomena have been suggested as capable of a new and plausible interpretation if atoms are considered as capable of altering their volume through a wide range; namely, the heat of chemical reaction, adsorption, adhesion, and cohesion; ordinary solution; electrolytic solution; electrolytic dissociation; the passage of electricity through solids, liquids and gases; the nature of cathode rays (and probably also X rays and radium); the laws of Faraday and Dulong and Petit; false and true equilibrium; heat capacity and thermal expansion; quantivalence; stereo-chemistry and crystal form; and the critical phenomena.

Following papers will be devoted to a development, quantitative where possible, of these applications, as well as of many others. Unless further study reveals discrepancies, which have hitherto been concealed, I expect to be able to show: —

1. That the conception is not inconsistent with the two laws of energy.

2. That it conflicts with none of the quantitative conclusions of the atomic hypothesis, nor with the kinetic theory of gases, if heat be assumed to be due to mechanical energy operating upon atomic inertia.

3. That it is able to interpret the actual deviations of gases from the gas law better than any other theory, retaining the essential import of

the equation of van der Waals, and modifying this equation only as regards the changeability of a and b.

4. That it is consistent with the varying specific heats of substances in the solid, liquid, and gaseous states.

5. That with the help of this theory such physical properties as tenacity, ductility, malleability, and coefficient of expansion assume for the first time a conceivable consisteney.

6. That upon it may be based a definition of the essential influences of chemical change and equilibrium.

7. That the variable compressibility of atoms furnishes a plausible explanation for many of the phenomena of quantivalence, including even the feeble affinities holding water of crystallization and other so-called molecular combinations.

8. That it explains all the tridimensional relations of material, such as stereochemistry and crystal form, at least as well as any other theory.

9. That with the proviso that electrical energy is a rhythmic manifestation of energy, — tending to repel itself and therefore to keep upon the surface of material which is susceptible to it, and hence to expand a free atom, — many of the electrical and magnetic phenomena of matter become more conceivable.

10. That the effect of light in hastening the attainment of chemical equilibrium, and the possibility of storing and emitting light energy possessed by material, may be interpreted in a similar way.

11. That the careful consideration of all these and other facts leads to a somewhat new conception of the relation between gravitation and chemical affinity, as well as between matter and luminiferous ether. This conception involves simply an antithesis of contracting and expanding tendencies, and is thus founded entirely upon an energetic basis.

12. That the idea is capable of throwing light upon the periodic system, and the genesis and permanence of the elements.

13. That it may be applied even to such astrophysical problems as the cause of the sun's heat.

This is a large program; some of it is already in manuscript, and more must await further exact experiment. The program is given here only to call attention to the wide possibilities of the consistent introduction of the conception of atomic compressibility into chemistry and molecular physics.

The present paper is only one step in the direction indicated. It is nevertheless an important step, for it adds approximate quantitative evidence to the previously given qualitative evidence concerning the significance of changing atomic volume.

III. Summary.

The contents of the paper may be divided into two parts: In the first part is set forth an approximate generalization which rests upon facts alone. This part of the paper can be overthrown only by the proof that the facts upon which it rests are erroneous. In the second part of the paper a plausible hypothetical interpretation of the facts is given. This part of the paper stands ready to share the fate of all hypotheses, — namely, to retire into oblivion if it is not capable of aiding the discovery of truth.

In brief, the chief points touched upon may be summed up as follows: —

I. (*a*) It has been shown that the contraction exhibited during chemical combination is in many cases approximately proportional to the heat evolved.

(*b*) Upon correcting the results for known differences of compressibility, the approximation becomes closer.

(*c*) An approximate calculation of the work which would probably be involved by the compression of a gram-atom each of sodium and chlorine into the space occupied by a gram-molecule of salt showed this work to be of the same order of magnitude as the actual heat of formation.

(*d*) From these facts and calculations the inference is drawn that the heat of chemical reaction is chiefly due to the energy required for the compression which takes place in the reaction.

(*e*) Possible corrections are pointed out.

(*f*) An explanation is given upon the same basis of the mechanism of the heat of adsorption, adhesion, and change of allotropic form.

II. (*a*) While the evidence is not exact, it affords a strong presumption in favor of the hypothesis of compressible atoms. The possibly far-reaching effect of this simple and plausible hypothesis upon chemical theory is pointed out.

(*b*) There is given a list of the especially prominent aspects of the question which will form the subjects of immediate experimental and theoretical study in this Laboratory.

Cambridge, Mass., U. S. A.